Waste to wealth: hydrothermal liquefaction of agricultural and forestry wastes into value-added chemicals

Hydrothermal liquefaction has been widely applied to obtain bioenergy and high -value chemicals from biomass in the presence of a solvent at moderate to high temperature (200 °C to 550 °C) and pressure (5 MPa to 25 MPa).

Biomass generally refers to organic substances (except fossil fuels and their derivatives), including plants, animals, microorganisms, as well as organic materials derived from excretion and metabolisms of these organisms, such as agricultural and forestry residues, aquatic plants, urban life, and industrial organic wastes. As typical lignocellulosic biomass, agricultural and forestry wastes are primarily composed of cellulose, hemicellulose, and lignin.

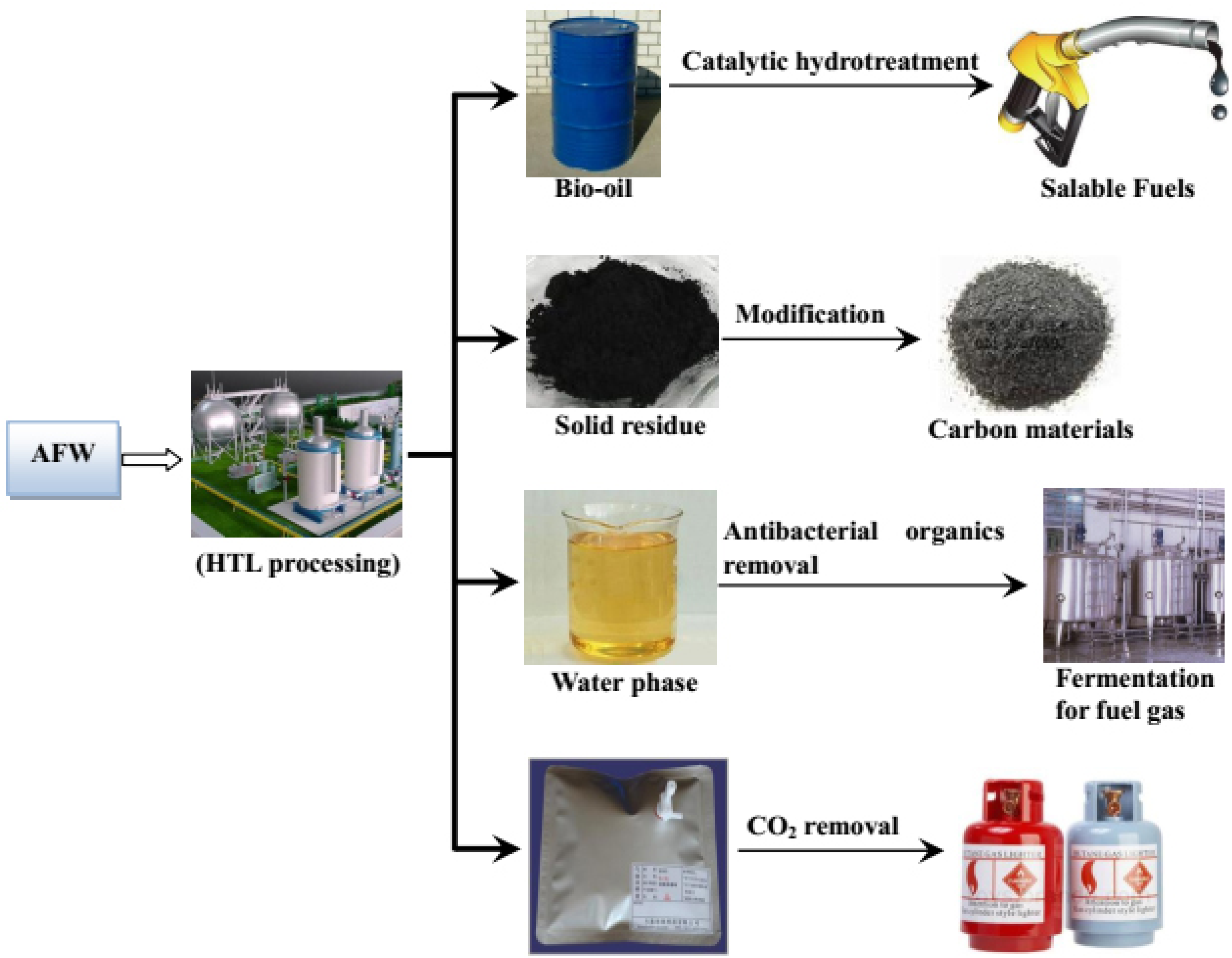

Fig. 1. Scheme of a biorefinery using hydrothermal liquefaction processing and agricultural and forestry wastes (AFW).

In a typical HTL process, lignocellulosic materials are depolymerized into bio-oil, biogas, biochar, and water-soluble matter in an aerobic or anaerobic enclosure (Fig. 1). Purified bio-oils can be used as fuels for burners, stationary diesel engines, turbines and boilers. Bio-oils can also be further upgraded into transportation fuels (diesel and gasoline) and products, including aromatics, polymers, asphalt, and lubricants.

Cellulose is the largest component of lignocellulosic materials, followed by hemicellulose and lignin (Fig. 2). The structure of cellulose is stable as it is organized into microfibrils surrounded by hemicellulose and encased inside a lignin matrix in the real biomass. Cellulose is firstly degraded into monosaccharides and oligosaccharides under the action of water and the decomposed monosaccharides are converted into furan derivatives when the HTL temperature increases. Aldehyde and small molecule acids are also produced when the temperature further increases.

Hemicellulose, which is composed of a variety of sugars including xylose, glucose, mannose, and lactose, comprises 20% to 40% components of biomass (Fig. 2). The composition of hemicellulose varies for different biomass. The hemicellulose of herbaceous plants mainly consists of xylan, whereas that of woody plants mainly consists of mannose, glucose, and chitosan. Because of its branched chains and poor structural regularity, the crystallinity of hemicellulose is weaker than that of cellulose. At temperatures above 120 °C, hemicellulose is easily hydrolyzed, which can be catalyzed by both acid and alkali. During the hydrolysis of hemicellulose, the decomposition reactions of sugars also occur, which are similar to the hydrolytic process of cellulose. At high temperatures, a variety of small molecules can be produced from xylose through dehydration and acetylation.

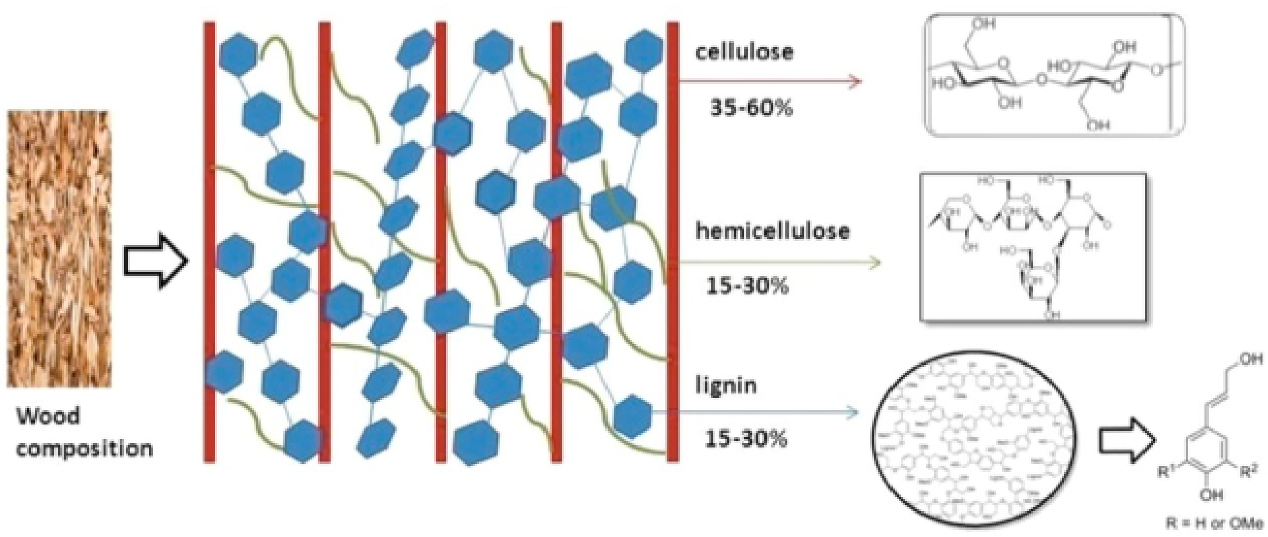

Fig. 2. Main components of lignocellulosic biomass and their chemical structures.

Lignin is a heterogeneous aromatic biopolymer that accounts for nearly 30% of the organic carbon on Earth, and is one of the few renewable sources of aromatic chemicals that exist in agricultural and forestry residues (Fig. 2). Lignin is the second most abundant natural polymer, next to cellulose, and exists in large amounts in plants cells and wood tissues. Hydrothermal liquefaction is an approach for lignin conversion into low-molecular-weight chemicals. Depending on the reactor design and operating conditions lignin can be fragmented into a series of phenolic derivatives and/or converted further into H_2, CO, CO_2, CH_4, C_2H_6, and other low-molecular-weight fragments.

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